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состояния системы Не³ — Не⁴. В связи с этим были поставлены новые опыты по измерению упругости пара растворов, результаты которых излагаются в настоящей статье.

2. Прибор и метод измерений

Как показали предварительные опыты, правильное измерение упругости пара растворов Не³ в Не⁴ возможно только при соблюдении некоторых предосторожностей. Наиболее существенными здесь являются строгое постоянство температуры и установление равновесия между паром и жидкостью. Кроме того, чтобы концентрацию Не³ в жидкости можно было считать равной концентрации Не³ в неохлажденном газе, необходимо использовать по возможности большое количество жидкости, а объем газовой фазы свести до минимума. Наконец, ниже λ-точки существенную роль могут играть эффект ползания пленки Не II, ее испарение и конденсация образовавшегося газа. Повышенное давление, возникающее при реконденсации, зависит от скорости переноса жидкого гелия по пленке, причем эта скорость значительно возрастает, если стенки прибора покрыты слоем твердых примесей [13], т. е. если конденсировался грязный гелий. Таким образом газ перед конденсацией необходимо очищать от всех примесей.

Все эти соображения были учтены при конструировании прибора. схема которого представлена на рис. 1. Он состоит из двух стеклянных толстостенных капилляров *a* и *b* с диаметром отверстия 0,7 мм, переходящих внизу в тонкостенные шарики *c* и *d* диаметром 10 мм. Вверху к этим капиллярам припаивался масляный дифференциальный манометр *M*, которым определялась разность упругостей пара между раствором и Не³. Вакуумные краны S_1, S_2, S_3 и S_4 позволяли производить конденсацию смеси в одном шарике, а Не³—в другом, отсоединять на время конденсации манометр от шариков и присоединять его к ним после окончания конденсации. Кран S_5 служил для соединения обеих частей манометра, что облегчало откачку прибора перед опытом. В каждом из шариков помещалась очень легкая железная вертушка, которая приводилась в колебательное движение при вертикальном перемещении постоянного магнита *N*. Последнее осуществлялось при помощи кривошипа *K*, вращаемого электромотором со скоростью 12 об / мин. Все это устройство предназначалось для перемешивания жидкости во время опыта, чем достигалось быстрое установление равновесия между паром и жидкостью. Нижняя часть прибора для защиты от теплоизлучения была окружена медным экраном *P*, в котором имелись две узкие щели для наблюдения за уровнем гелия в шариках *c* и *d*.

Рис. 1. Прибор для измерения упругости пара растворов Не³ в Не⁴

Опыт велся следующим образом. После тщательной откачки прибора закрывались все краны, и дьюар заполнялся жидким гелием. Затем температура жидкого гелия понижалась откачкой до ~ 1.35°К, и производилась конденсация Не⁴ в одном шарике и смеси в другом. Предварительно оба газа проходили через змеевики, охлажденные жидким водородом, а смесь проходила еще дополнительно через змеевик, погруженный в жидкий гелий, имевший температуру 4,2°К.
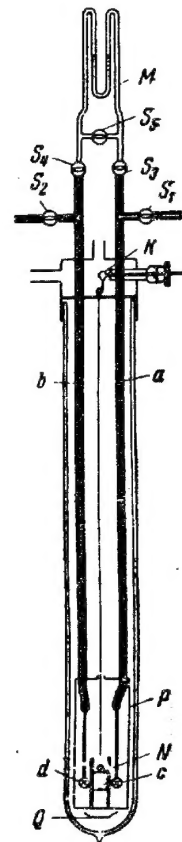
на себя внимание тот факт, что имеют место положительные и отрицательные отклонения кривой упругости пара от такой же кривой для идеального раствора, причем температура, при которой происходит пересечение экспериментальной кривой с кривой для идеального раствора, закономерно меняется с концентрацией. Это
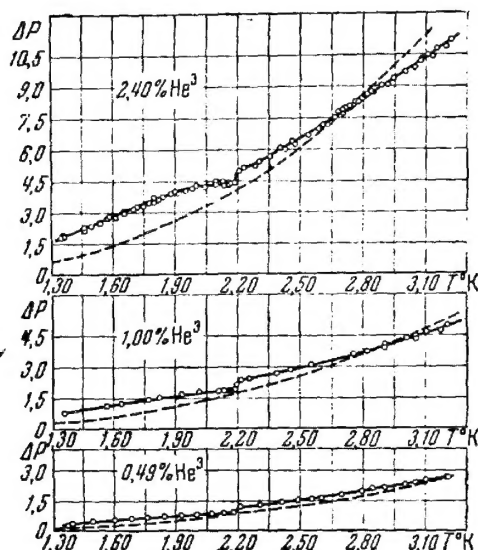

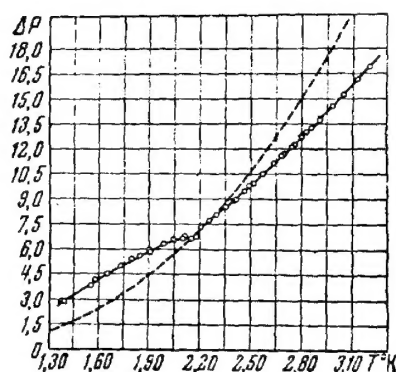Рис. 2. Зависимость ΔP (мм рт. ст.) от температуры для растворов с концентрацией He³ 0,49; 1,00 и 2,40%

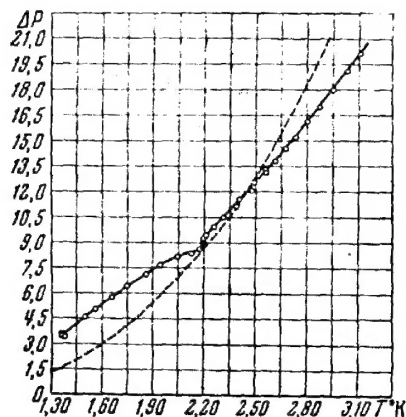Рис. 3. Зависимость ΔP (мм рт. ст.) от температуры для раствора с концентрацией He³ 4,23%

Рис. 4. Зависимость ΔP (мм рт. ст.) от температуры для раствора с концентрацией He³ 5,18%
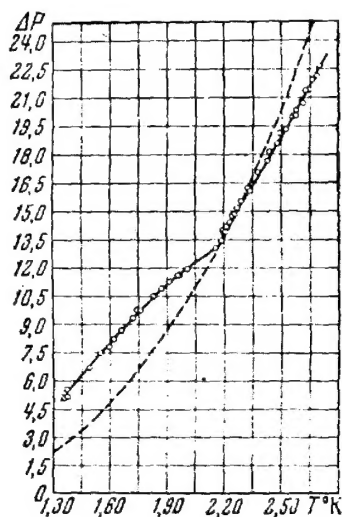
Рис. 5. Зависимость ΔP (мм рт. ст.) от температуры для раствора с концентрацией He³ 8,08%

отчетливо видно из рис. 6, на котором изображена зависимость температуры пересечения кривых от концентрации. Вертикальными линиями изображены ошибки в определении температуры пересечения кривых, являющиеся следствием ошибок в определении концентрации He³ в неохлажденном газе.

На рис. 7 и 8 представлены изотермы давления пара растворов как функции состава жидкой фазы, полученные из предыдущих кривых.

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Как и раньше, пунктиром изображена аналогичная зависимость для идеальных растворов. Указанные положительные и отрицательные отклонения от кривых для идеального раствора здесь отчетливо видны.
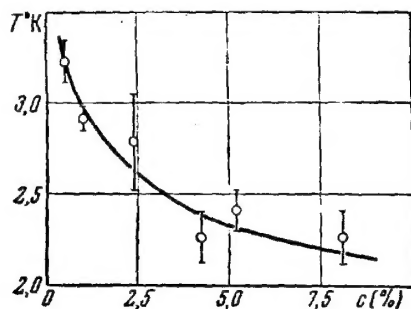

Рис. 6. Зависимость температуры пересечения экспериментальной и идеальной кривых от концентрации He[3] в растворе
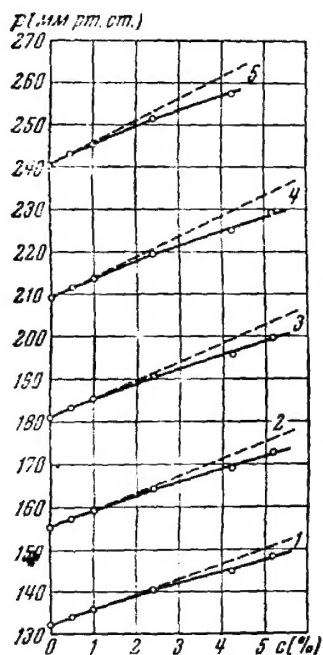
Рис. 7. Изотермы давления пара растворов He[3] в He[4] как функции состава жидкой фазы. 1—2,80°; 2—2,90°; 3—3,00°; 4—3,10°; 5—3,20° К
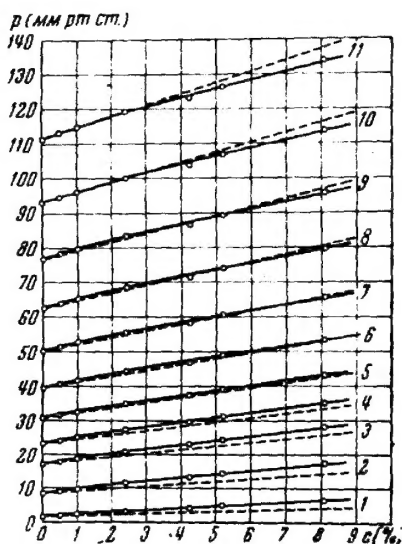
Рис. 8. Изотермы давления пара растворов He[3] в He[4] как функции состава жидкой фазы. 1—1,35°; 2—1,70°; 3—1,90°; 4—2,00°; 5—2,10°; 6—2,20°; 7—2,30°; 8—2,40°; 9—2,50°; 10—2,60°; 11—2,70° К

4. Обсуждение результатов

Полученные результаты дают возможность сделать вывод о том, что растворы He[3] в He[4] не являются идеальными растворами ни ниже, ни выше λ-точки. При этом, однако, надо иметь в виду следующее. Обычно под идеальным раствором подразумевается система, для ко-

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CERTAIN PROPERTIES OF SOLUTIONS OF He^3 in He^4

III. VAPOUR PRESSURE

(Reported by B. N. YESEL'SON)

[744]

The vapour pressure of solutions of He^3 in He^4 is measured in conditions, guaranteeing establishment of an equilibrium between the liquid and the vapour. The data, obtained for solutions of 0.49; 1.00; 2.40; 4.23; 5.18 and 8.08% He^3, permit a conclusion to be made about the unideal behaviour of such solutions.

1. Introduction

Together with the other properties of solutions of He^3 in He^4, the relation between the vapour pressure of such solutions and the composition of the liquid and gaseous phases is of interest. The existence of such data would allow of the construction of a diagram of state of the system $He^3 - He^4$, the knowledge of which is essential for improving the technique of separating the helium isotopes [1]. Moreover a diagram of state of the system $He^3 - He^4$, from the point of view of a general study of solutions of two isotopes, is of real interest.

A series of works [2-12] deal with the measurement of the vapour pressure of solutions of He^3 in He^4 and the determination of the coefficient of distribution of He^3 between the liquid and the vapour. However up till the present there is still no reliable data relating either to vapour pressure or the coefficient of distribution. This is explained by the fact that in the majority of experiments connected with the measurement of the vapour pressure of solutions, a small quantity of the mixture was used, and also there was no certainty that the concentration of He^3 in the liquid was equal to that in the uncondensed gas. Apart from this, the establishment of an equilibrium between the vapour and the liquid was not controlled in any experiment, nor were any measures taken for a quick establishment of this equilibrium. Finally, measurements of vapour pressure in the HeII sphere, apparently, are always disturbed because of the effect of the film, with which these disturbances can be particularly large, if the corresponding precautionary measures are not taken. As a result of this the data obtained up till the present both in the sphere of HeII and that of HeI are for the most part incorrect.

/Matters

Matters are no better as regards the measurement of the coefficient of distribution. Attempts to determine this by means of selection and analysis of samples of vapour were unsuccessful. The basic difficulty, which must be overcome here is that in the HeII region, the vapour sample, in spite of a number of precautions, appears as /weak/ He^4 due to the transport of HeII along the film. Above the λ point the data obtained are scarcely reliable, since in selecting the sample the presence of an equilibrium, between the liquid and vapour, which in this range of temperatures is established slowly, was not controlled.

Thus at the present there is still insufficiently reliable data from which to draw a diagram of state of the system He^3 - He^4. For this reason new experiments were made to measure the vapour pressure of solutions the results of which are given in this paper.

2. Apparatus and method of measurement

As the previous experiments showed, correct measurements of the vapour pressure of solutions of He^3 in He^4 is possible only if certain precautions are observed. A strict constancy of temperature and the establishment of an equilibrium between the vapour and liquid are essential. Moreover, in order that the concentration of He^3 in the liquid can be considered equal to the concentration of He^3 in the uncondensed gas, it is essential to use as large a quantity of liquid as possible, and to reduce the volume of the gaseous phase to a minimum. Finally below the λ point a significant part can be played by the effect of creep of the HeII film, its evaporation and the subsequent condensation of the gas. The increased pressure, arising on recondensation, is related to the speed of transfer of the liquid helium through the film, and this speed increased significantly if the sides of the apparatus are covered by a layer of solid impurities [13] i.e. if the impurities in the helium have condensed. Thus it is essential to free the gas from all impurities before condensation.

All these considerations were taken into account in constructing the apparatus, the arrangement of which is shown in Fig. 1. It consists of two thick sided glass capillaries a and b with bore diameter 0.7 mm. connected at the bottom with two thin sided bulbs c and d 10 mm in diameter. To the top of these capillaries a differential oil manometer was fixed with which

we determined the difference of vapour pressure between the solution and
He^4. The vacuum taps S_1, S_2, S_3 and S_4 allowed us to carry out condensation
of the mixture in one bulb and He^4 - in the other, and to disconnect the
manometer from the bulbs during condensation and to connect it to them after
completion of condensation. The tap S_5 served to connect both parts of the
manometer together which facilitated the evacuation of the instrument before
the experiment. In each of the bulbs we placed a very light iron stirrer,
which was given an oscillating motion by vertical movement of the permanent
magnet M. The latter was accomplished with the aid of a crank K turned by
an electric motor with a speed of 12 revs/min. All this equipment was
designed for agitating the liquid during the test, by which a quick
establishment of an equilibrium between the liquid and vapour was achieved.
The lower part of the apparatus was protected from heat irradiation by
surrounding it with a copper screen, in which there were two narrow slots
for observing the level of helium in the bulbs c and d.

The experimental procedure was as follows. After careful evacuation
of the apparatus all taps were closed and the Dewar was filled with liquid
helium. Then the temperature of the liquid helium was lowered by
evacuation to $\sim 1.35^{\circ}$K, and condensation of He^4 in one bulb and the mixture
in the other took place. Previously both gases were passed through spiral
tubes cooled by liquid hydrogen, and the mixture was further passed through
a spiral tube, immersed in liquid helium having a temperature of 4.2°K.

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As a result of such procedure all impurities froze in the spiral tubes and
both gases entered the apparatus completely pure. In each of the bulbs
about 400 cm^3 of gas was condensed, so that they were almost completely
filled with liquid.

After completion of condensation the manometer was connected with the
bulbs and when equilibrium was attained between the vapour and liquid the
difference of heights of the levels of the oil in them, corresponding to the
difference of vapour pressure (ΔP) of the solution and He^4, was measured
with the aid of a cathetometer. The approach to equilibrium between the
liquid and vapour was determined by the constancy of ΔP over a period of
time. Equilibrium was indicated below the λ-point after a period of
3-4 mins. even without agitation of the liquid. In the HeI zone

equilibrium without agitation was established after a time measured in hours,

/but

but with agitation after 10-15 mins.   From this it is obvious that such
agitation, used normally in experiments with solutions, is also very
essential in work with solutions of He^3 in He^4, though several authors
consider this unnecessary.

Warming the helium in the Dewar with the aid of the heater Q made it
possible to find the relation of ΔP to temperature.   On reaching the desired
temperature the pressure in the Dewar was again kept constant.   An analogous
relation was determined after this during lowering of the temperature.

The apparatus was tested during condensation of He^4 in both bulbs.
Here ΔP was zero above or below the λ-point whether the liquid was
agitated or not.   An analogous result was obtained with a stirrer in one
bulb only.   From this it followed that, the heat, given off during
oscillation of the stirrers, is so small that it does not noticeably affect
the measured ΔP.   As the volume of the instrument was small (about 5 cm^3),
then the errors arising from condensation of not less than a fixed quantity
of the mixture due to impoverishment of the solution through transfer of part
of He^3 to the gaseous phase, were not great.   The latter was specially
determined by studying the relation of ΔP to the quantity of the condensed
mixture, when at all temperatures, down to $3.2^{\circ}K$, it was less than the
normally condensed 400 cm^3.[1]

3. Results

With the aid of the apparatus described we determined the relation of
ΔP to temperature for solutions with content of 0.49; 1.00;   2.40;   4.23;
5.18 and 8.08% He^3.   The results obtained are shown in Figs. 2-5, whilst
on the same figures the calculated relation of ΔP to temperature, resulting
from the assumption of the idealness of solutions of He^3 in He^4, is shown
by a dotted line.   In this case we have

$$\Delta P = c_3^L (P_3^0 - P_4^0) \qquad - \quad - \quad - \qquad (1)$$

where c_3^L is the concentration of He^3 in the liquid and $P_3^0 \& P_4^0$ are the
vapour pressures of pure He^3 and He^4 respectively.   For solutions with the
given content of He^3, as can be seen from Figs. 2-5, ΔP increases as the
temperature increases whilst at the λ-point for He^4 one observes a change of

/sign

sign of the curve and a rapid increase of ΔP. The experimental points on
all curves were obtained as a result of going through every temperature
interval both up and down. The lack of hysteresis again supports the fact
that in the course of all experiments an equilibrium existed between the
/14/ vapour and the liquid. Ones attention is attracted by the fact that there
are positive and negative deviations of the curve of vapour pressure from
the corresponding curve for an ideal solution, whilst the temperature at
which the experimental curve crosses the curve for an ideal solution changes
regularly with the concentration. This is clearly seen from Fig. 6 on which
the relation of the temperature of crossing to the concentration is shown.
The vertical lines show the errors in determining the temperatures of
crossing the curves, being the result of errors in determining the
concentration of He^3 in the uncondensed gas.

Figs. 7 and 8 give the isotherms of vapour pressure of solutions, as a
function of the composition of the liquid phase, obtained from the foregoing.
/14/ As before the analogous relation for ideal solutions is shown in broken lines.
The positive and negative deviations from curves for an ideal solution
mentioned above can be clearly seen here.

4. Review of Results

The results obtained make it possible to conclude that solutions of He^3
in He^4 are not ideal solutions either below or above the λ-point. However
the following should be borne in mind. Normally by an ideal solution one
/14/ means a system for which additivity of thermodynamic values takes place
(with errors not exceeding the entropy of displacement) namely:

$$E = E_1 + E_2$$
$$W = W_1 + W_2$$
$$S = S_1 + S_2 + N_1 k l_n \frac{N}{N_1} + N_2 k l_n \frac{N}{N_2} \quad - \quad -- \quad (2)$$
$$\bar{\phi} = \bar{\phi}_1 + \bar{\phi}_2 + N_1 \overline{kT} l_n \frac{N_1}{N} + N_2 \overline{kT} l_n \frac{N_2}{N}$$

where E, W, S and $\bar{\phi}$ are energy, heat function, entropy and thermodynamic
potential of the mixture respectively, N is the total number of particles
in the mixture; the same values with suffixes 1 and 2 refer to the
components of the mixture.

The physical reason leading to this is the supposed equivalence of
reaction between different and identical particles in the sense that the
displacement of the particles in the solution does not change the energy

/levels

and HENRY follow from the expressions (2___). For isotopes, as is well known, from the stated assumptions in the classic approximation it follows that the vapour pressures of these isotopes will not differ [14]. However in calculating quantum effects with accuracy to terms in h^2 there follows a variation in the vapour pressure for isotopes, whilst the relationships (2), expressing the properties of ideal solutions, continue to remain accurate. In accurate calculations (i.e. with calculation of the terms beyond h in the expansion) the isotope solution is not ideal in the sense of fulfilling the original expression (2). In particular, the laws of RAOULT and HENRY need not be fulfilled for it.

Thus, if one takes the expression (2) as determining the idealness of solutions, then even if the assumption of the equality of energy interchange between unlike and like particles is true the solution will not be ideal in the region of powerful quantum effects.

The experimental data obtained are compared in practice with the data for ideal solutions (1). The observed deviations from this idealness are

characterised by very interesting quantum effects, taking place in solutions of He^3 in He^4. Unfortunately at the present time there is no

2. It is shown that these solutions are not ideal either above or below the λ- point.

3. It was found that for solutions of He^3 in He^4 there are positive and negative deviations of the curve for vapour pressure from the same curve for an ideal solution.

In conclusion I express my thanks to B. G. LAZAREV and N. Ye. ALEKSEYEVSKI for valuable advice, and to I. M. LIFSHITS and Ye. S. BOROVIK for reviewing the results obtained.

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Captions to figures

1. Apparatus for measuring vapour pressure of solutions of He^3 in He^4.

2. Relation of ΔP (mm. mercury column) to temperature for solutions with 0.49, 1.00 and 2.40% concentration of He^3.

3. Ditto concentration of He^3 4.23%.

4. Ditto concentration of He^3 5.18%.

5. Ditto concentration of He^3 8.06%.

6. Relation of temperature of intersection of experimental and ideal curves to concentration of He^3 in solution.

7. Isotherms of vapour pressure of solutions of He^3 in He^4 as a function of the composition of the liquid phase. 1 - 2.80°; 2 - 2.90°; 3 - 3.00°; 4 - 3.10°; 5 - 3.20°K.

8. Ditto 1 - 1.35°; 2 - 1.70°; 3 - 1.90°; 4 - 2.00°; 5 - 2.10°; 6 - 2.20°; 7 - 2.30°; 8 - 2.40°; 9 - 2.50°; 10 - 2.60°; 11 - 2.70°K.